

Thallium, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Thallium, dissolved, I-1866-85 ($\mu\text{g/L}$ as Tl): 01057

1. Application

This method may be used to analyze water containing at least $1 \mu\text{g/L}$ of thallium. Samples containing more than $9 \mu\text{g/L}$ need either to be diluted or a smaller volume needs to be used for analysis.

2. Summary of method

2.1 Thallium is determined by atomic absorption spectrometry in conjunction with a graphite furnace and the method of standard additions. The sample is placed in the graphite tube and is then evaporated to dryness, charred, and atomized. The absorbance signal generated during atomization is recorded. Known concentrations of thallium are added to aliquots of the sample in the tube and the technique is repeated. The absorbances are then plotted and the concentration of thallium is determined by extrapolation.

2.2 Pretreatment of the graphite tube with ammonium molybdate and addition of ammonium nitrate to the sample in the graphite tube are employed to reduce background scattering.

2.3 For discussion of standard additions, see this chapter, Analytical techniques, atomic absorption spectrometry.

3. Interferences

False peaks or recorder deflections below the baseline often occur during the atomization cycle because of heavy background scattering in this wavelength region (276.8 nm) and because of the requirement for very close alignment of the deuterium background corrector and source (electrodeless-discharge lamp).

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use

at 276.8 nm , equipped with deuterium background correction, graphite furnace, and recorder with 2.5-mv or 5.0-mv range.

4.2 Refer to the manufacturer's manual to optimize instrumental performance.

4.3 *Graphite furnace*, capable of reaching temperatures sufficient to atomize thallium. CAUTION: Dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration. Use the following operating conditions:

Drying temperature ----- 100°C

Charring temperature ----- 400°C

Atomizing temperature --- 2400°C

Drying time ----- (NOTE 1)

Charring time ----- 15 s

Atomizing time ----- 10 s

Purge gas----- Argon, $25 \text{ cm}^3/\text{min}$
normal flow

NOTE 1. Set drying time for as many seconds as the total microliters of sample plus standard injected.

4.4 *Graphite tubes*, compatible with furnace. Standard graphite tubes are preferred.

4.5 *Pipets*, microliter with disposable tips, 1- to $50\text{-}\mu\text{L}$ capacity.

4.6 *Thallium light source*, thallium electrodeless-discharge lamp.

4.7 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Ammonium hydroxide solution*, 3M: Dilute 20 mL concentrated NH_4OH (sp gr 0.90) to 100 mL with demineralized water.

5.2 *Ammonium molybdate solution*, 8.7 g/50 mL: Dissolve 9.2 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in 40 mL 3M ammonium hydroxide solution and dilute to 50 mL with demineralized water.

5.3 *Ammonium nitrate solution*, 25 g/50 mL: Dissolve 25 g NH_4NO_3 in 50 mL demineralized water.

5.4 *Nitric acid*, concentrated (sp gr 1.41): High-purity, Ultrex or equivalent.

5.5 *Nitric acid solution*, (1 + 499): Mix 1 part concentrated HNO_3 (sp gr 1.41) with 499 parts demineralized water.

5.6 *Thallium standard solution I*, 1.00 mL = 1000 μg Tl: Dissolve 1.303 g TlNO_3 in demineralized water. Add 2 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.7 *Thallium standard solution II*, 1.00 mL = 20.0 μg Tl: Dilute 20.0 mL thallium standard solution I to 1,000 mL with nitric acid solution (1 + 499).

5.8 *Thallium working standards*: Dilute 50, 100, and 150 μL each of thallium standard solution II to 250 mL with nitric acid solution. These working standards represent concentrations of 4, 8, and 12 $\text{pg}/\mu\text{L}$ of thallium. Prepare fresh daily (NOTE 2).

NOTE 2. Clean the 250-mL volumetric flasks with dilute nitric acid (1 + 50) and rinse with demineralized water immediately before use. Rinse the 50- μL micropipet disposable plastic tip twice in a solution of nitric acid (1 + 2), twice in demineralized water, and twice in thallium standard solution II before preparing the working standards.

6. Procedure

6.1 Prior to use, rinse pipet tips twice with a solution of nitric acid (1 + 2) and then twice in demineralized water.

6.2 Pretreat the graphite tube. Inject 25 μL ammonium molybdate solution and cycle as follows: dry for 20 s at 110°C, char for 15 s at 550°C, and atomize for 10 s at 2500°C. Use an argon flow of 12 mL/min in the interrupt mode. Repeat injection and cycle three times.

6.3 Inject 30 μL of sample into the graphite tube and dry, char, and atomize as given in step 4.3.

6.4 From the signal's peak height obtained in paragraph 6.3, choose a sample volume which

will give a signal less than 40 percent of full scale on the recorder.

6.5 Choose a volume of thallium working standards that, when added to the sample aliquot, will produce a 50-, 100-, and 150-percent increase in signal peak height (NOTE 3). Inject the same volume of demineralized water to the sample for the blank spike.

NOTE 3. To determine the approx. signal (absorbances or peak heights) of the thallium working standards, inject 30 μL of the low working standard, cycle, and record signal. From this information, the volume of standard can be determined.

6.6 Inject in the graphite tube the aliquot of sample and blank as determined in steps 6.4 and 6.5. Cycle as given in paragraph 4.3 and record absorbance or peak height. Repeat process with sample and the standard additions of thallium working standards as determined in steps 6.4 and 6.5. Analyze the sample plus standards twice (NOTE 4).

NOTE 4. If background interferences occur as mentioned in paragraph 2.2, inject 20 μL ammonium nitrate solution to each sample, standard, and blank.

7. Calculations

7.1 Plot absorbances (or peak heights) of sample plus standards on the vertical axis of a graph and the mass, in pg , added on the horizontal axis.

7.2 Fit the points to a straight line by the least-squares method and extrapolate the line to the horizontal axis. The mass of thallium present in the sample is the reading at the horizontal intercept.

7.3 Determine the micrograms per liter of dissolved thallium in each sample as follows:

$$\text{Tl}(\mu\text{g}/\text{L}) = \frac{\text{mass Tl in sample (pg)}}{\text{volume of sample} (\mu\text{L})}$$

8. Report

Report thallium, dissolved (01057), concentrations to the nearest microgram per liter.

9. Precision

9.1 Precision for dissolved thallium for four samples expressed in terms of the percent relative standard deviation is as follows:

Number of Laboratories	Mean ($\mu\text{g/L}$)	Relative standard deviation (percent)
4	3.2	75
5	3.4	38
6	3.8	39
3	5.0	20

9.2 Analysis of two samples six times each by a single operator resulted in mean values of 5.6 and 10.9 $\mu\text{g/L}$ and relative standard deviations of 10 and 3 percent, respectively.